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Effect of TiO_2 Incorporated with Al_2O_3 on the Hydrodeoxygenation and Hydrodenitrogenation CoMo Sulfide Catalysts

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Abstract

The influence of TiO_2 incorporation in Al_2O_3 support was investigated in the catalytic activity of hydrodeoxygenation (HDO) and hydrodenitrogenation (HDN) reactions. Alumina–titania supported CoMo sulfide catalysts (mole ratio 1:0, 1:0.25, 1:50, 1:0.75, and 0:1) were prepared by sol-gel method. The CoMo sulfide catalysts were characterized by BET, NH_3-TPD, H_2-TPR, XRD and TEM techniques. Guaiacol and quinoline were used as model compounds in HDO and HDN reactions, respectively. The liquid products were examined by GC-FID and GC-MS. The results suggest that TiO_2 incorporated Al_2O_3 support obviously involves the catalytic activity on the HDO and HDN reactions. The role of the partial incorporation of TiO_2 into Al_2O_3 was discussed.

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Keywords: Hydrodenitrogenation, hydrodeoxygenation, sulfide catalysts, Al_2O_3-TiO_2 support, CoMo catalysts

1. Introduction

Bio-oil derived from fast pyrolysis of lignocellulosic biomass contains significantly quantities of several oxygen compounds, mostly in the form of phenolic compounds with some nitrogen compounds. As an alternative transportation fuels, bio-oil upgrading using hydrotreating process is necessary in order to dramatically remove the oxygen content through hydrodeoxygenation (HDO) reaction. The elimination

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of nitrogen compounds during the hydrotreating process via hydrodenitrogenation (HDN) is also important process because nitrogen compounds poison and deactivate the catalyst. The conventional catalysts for hydrotreating process are CoMo and NiMo supported on Al_2O_3. Al_2O_3 support provides high surface area and high thermal stability [1], however, as mentioned earlier, TiO_2 supported molybdenum catalysts has attracted considerable attention catalysts due to these catalysts exhibit the higher hydrotreating activities compared to Al_2O_3 supported molybdenum catalysts. However, the disadvantages of TiO_2 are low surface area, low thermal stability and poor mechanical property causing negative effect for long-term stability [2].

This work is to study the effect of the incorporating TiO_2 to Al_2O_3 support. The catalytic activities tested by HDO and HDN reaction as a function of TiO_2 content were investigated

2. Experimental

2.1 Preparation of catalysts

The 10%Mo/Al_2O_3-TiO_2 catalysts were prepared by the sol-gel method at varying the molar ratios of Al_2O_3 to TiO_2; 1:0, 1:0.25, 1:0.50, 1:0.75, 1:1, and 0:1. Then, the catalysts were dried at 50 ˚C for 48 h and calcined at 550 ˚C for 4 h. Afterward, the addition of 3% Co in the catalyst powder by using impregnation method, followed by dried 50 ˚C for 48 h and calcined at 550 ˚C for 4 h. The 3%Co10%Mo/Al_2O_3-TiO_2 catalysts denoted as 310CMAT(x:y), where (x:y) are mole ratio (1:0.5,1:0.75 and 1:1), whereas alumina and titania used as support designed as 310CMA and 310CMT, respectively .

2.2 Characterization

The surface area, pore volume and average pore diameter were characterized by N_2 adsorption using BELSORP:MINI II. The reducibility and acidity of catalysts were analyzed by temperature programmed reduction of hydrogen (H_2-TPR) and temperature programmed desorption of ammonia (NH_3-TPD), respectively using BELCAT-B. The phase identification of catalysts was confirmed by X-ray diffraction (XRD) using X-ray diffractomer (Rigaku TTRAX III). Finally, the morphology of MoS_2 catalysts was evaluated by TEM technique analyzed by JEOL, JEM-2010.

2.3 Catalytic activity test

Before the hydrotreatment test, the catalysts were sulfidized in a fixed bed reactor under the H_2S atmosphere. The HDO and HDN activities were carried out in a high temperature and pressure batch reactor (Parr 4848) at 300 °C under hydrogen pressure 50 bar for 2 h. The model compounds used as a feedstock for the catalytic activity testing consist of 5.00 wt.% guaiacol (a model of phenolic compound), 0.30 wt.% quinoline (a model of nitrogen compound) and organic solvent (1,2,3,4-tetrahydronaphthalene and n-hexadecane). The liquid products were analyzed by Agilent 7890 gas chromatograph equipped with the flame ionization (FID) detector and Agilent 5975 gas chromatograph equipped with mass spectrometer (MS) detector

3.Results and Discussion

3.1 Catalyst characterization

Textural properties (Table 1) of the synthesized catalysts after calcination exhibit that 310CMA catalyst provides the specific surface area up to 249.32 m_2/g with the average pore size of 3.95 nm, while

the specific surface area of 310CMT is 67.14 m_2/g with the average pore size of 10.62 nm. Surface area of mixed Al_2O_3 and TiO_2 support decreases with increasing TiO_2 content but the average pore size slightly increases. The reason can be contributed to the incorporation of TiO_2 to the Al_2O_3 support [2].

Table 1. Textural properties of all catalysts

Catalysts	S_{BET} (m^2/g)	Average pore diameter (nm)	Pore volume (cm^3/g)	Acidic (mmol/g cat.)
310CMA	249.32	3.95	0.25	1.047
310CMAT(1:0.25)	255.52	4.97	0.32	0.61
310CMAT(1:0.5)	231.51	5.15	0.29	0.61
310CMAT(1:0.75)	181.51	5.00	0.22	0.67
310CMAT(1::1)	198.35	5.61	0.27	0.69
310CMT	67.14	10.62	0.18	0.28

TPR profile of alumina support (Figure 1a) shows two broad H_2 consumption signals related to octahedral and tetrahedral Mo^{6+} reduction ($Mo^{6+} \rightarrow Mo^{4+}$), while TPR profile of titania support (Figure 1f) shows inversely tetrahedral and octahedral Mo^{6+} reduction [3]. Interestingly, the appearance of shoulder signal ca. 500-600 °C for 310CMAT(0:1) and 310CMAT(1:1) catalysts probably relates to $Ti^{4+} \rightarrow Ti^{3+}$ surface titania cations reduction [4]

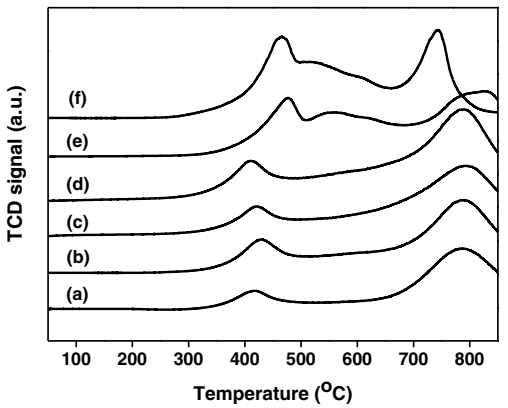

Fig. 1. TPR-profiles of (a) 310CMA (b) 310CMAT(1:0.25) (c) 310CMAT(1:0.5) (d) 310CMAT(1:0.75) (e) 310CMAT(1:1) and (f) 310CMT.

XRD patterns of three catalysts in Figure 2 observed only diffraction patterns of catalyst support. Alumina and titania supports exhibit the diffraction peaks belonging to the γ-Al_2O_3 and anatase TiO_2 phases, respectively, whereas 310CMAT(1:1) reveals anatase phase with low crystalline. This confirmed the incorporation of TiO_2 to Al_2O_3.

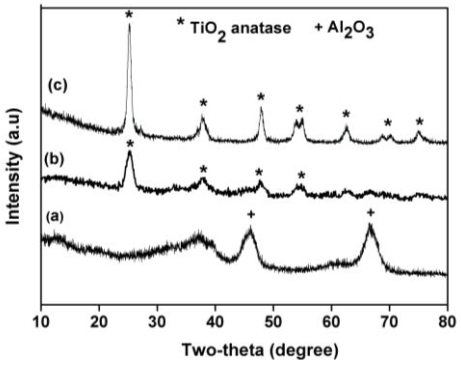

Fig. 2. XRD patterns of (a) 310CMA (b) 310CMAT(1:1) and (c) 310CMT.

The morphologies of the catalysts were revealed by TEM images as shown in Figure 3. These images display mainly the edge or planes of the MoS_2 slabs oriented on support along to the electron beam direction. The statistical distribution of the MoS_2 slabs in slab length and stacking number measuring from TEM images are presented in Figure 4. The effect of increasing TiO_2 into alumina support exhibits the increasing in the slab length causing by higher crystallite size of support, whereas increasing in stacking number due to its low metal-support interaction.

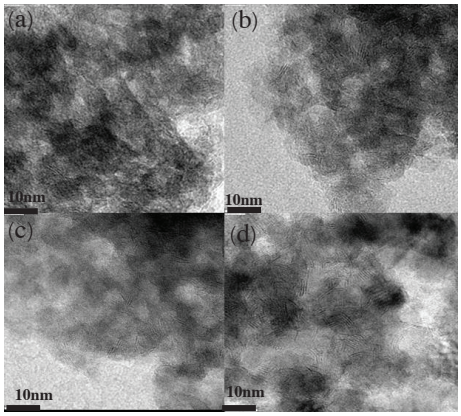

Fig. 3. TEM images of CoMoS in (a) 310CMA (b) 310CMAT(1:0.25) (c) 310CMAT(1:1). and (d) 310CMT.

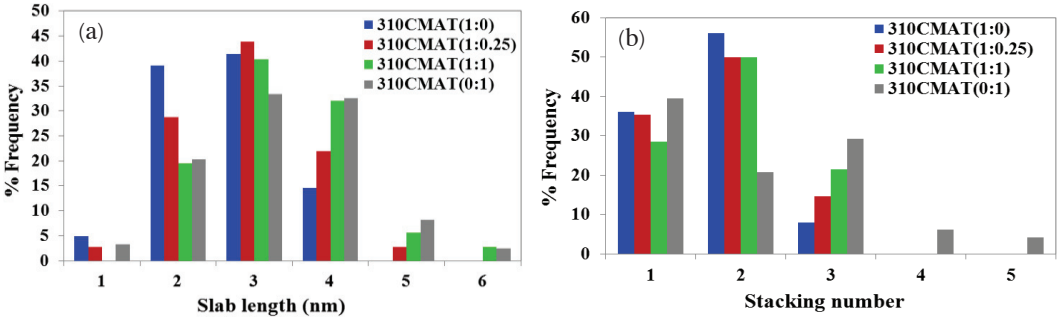

Fig. 4. Distribution of (a) Slab length and (b) stacking number

3.2 Catalytic activity test

Figure 5 shows the comparison of %HDO and %HDN reactions for all catalysts, which rather presents the linear relation of both reactions. At low TiO_2 content revealed the lower activity, while at high TiO_2 content appeared the higher activity comparing 310CMA catalyst. This indicated that the ratio of TiO_2-Al_2O_3 leading to catalytic activities. The % selectivity of liquid products occurred via the direct deoxygenation (DDO) and hydrogenation (HYD) is presented in Figure 6(a) according to their HDO pathways [5]. This displays that DDO products keep nearly constant, while HYD products change depending on TiO_2 content.

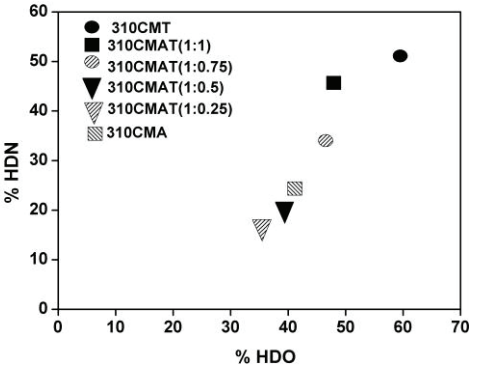

Fig. 5. HDO and HDN activity of the all catalysts at 300 °C under H_2 pressure 50 bar for 2h.

Above results can were elucidated by the rim-edge model [6], which the HYD partway only occurred on the top and bottom planes called rim-sites, whereas DDO partway occurred on the edge planes as illustrated in Figure 6(b). Therefore, TiO_2 content effect causes the amount of rim site exhibited in of sulfide MoS2 catalysts as described by TEM technique. Moreover, this indicated that the HYD active site is the important site for HDO reaction.

In addition, HYD site is also relation to HDN of quinoline, since HYD is first step for HDN of quinoline as shown in the mechanism in Figure 7(b). The liquid products from HDN of quinoline in Figure 7(a) reveal the results similar to HDO reaction.

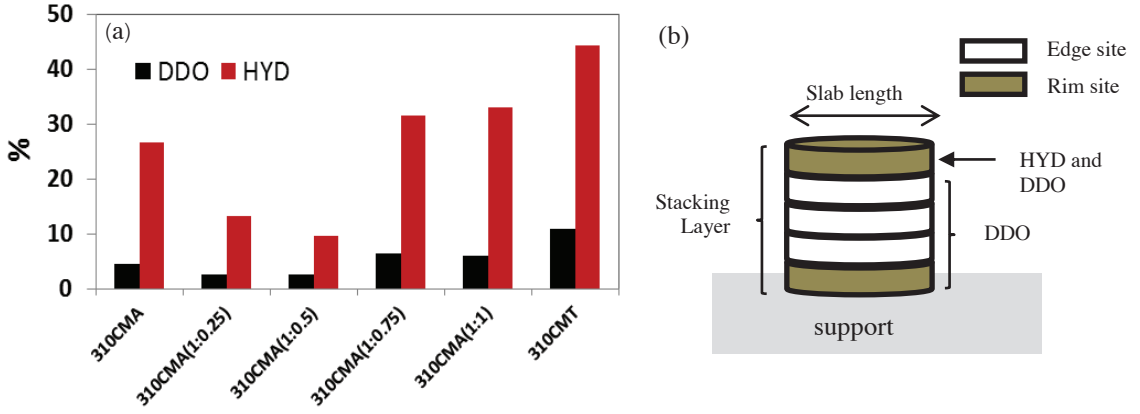

Fig. 6. (a) % product selective comparing DDO and HYD routes of guaiacol hyderdeoxygenation in the presence of quinoline at 300 °C under H_2 pressure 50 bar for 2h.and (b) rim-edge model of a MoS_2 catalysts particle.

Moreover, TiO_2 was considered as an electronic promoter in supported CoMo catalysts. The 3d electron in Ti^{3+} formed under the reducing conditions can be transferred through the Mo 3d conduction band, leading to weakening of the Mo–S bond and an increase in the number of coordinately unsaturated metal sites (CUS) [4]. Moreover, it also indicated that TiO_2 also is a promoter for HDN of quinoline, enhancing both the hydrogenation and C–N bond cleavage activities. Amount of HDN products (PCHA, PCHE, PB and PCH) increase with the increasing TiO_2 content.

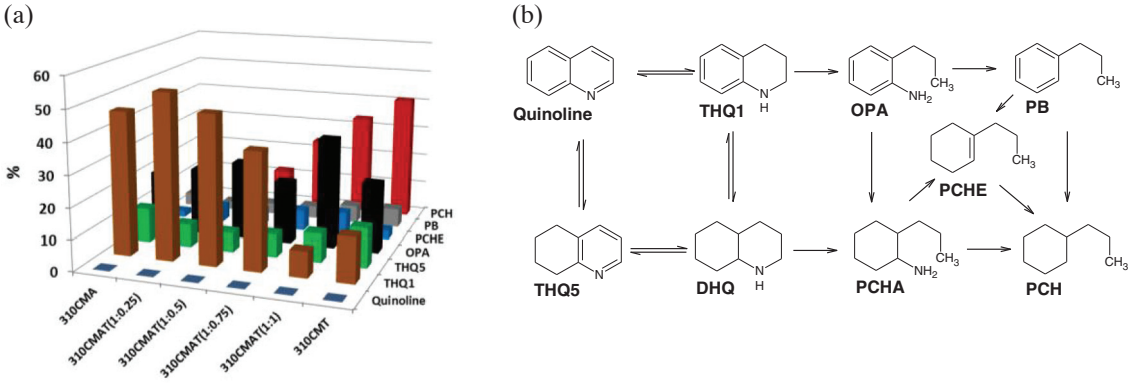

Fig. 7. (a) Distribution products of HDN from quinoline (b) scheme of generally reaction pathway for quinoline hydrodenitrogenation [7].

4. Conclusion

The TiO_2 incorporated with alumina on CoMo sulfide catalysts affects the structural and morphology MoS_2 catalyst leading to amount of rim site. In addition electronic effect of TiO_2 causes the enhance activity. Both effects play the importance role of HDO and HDN activities.

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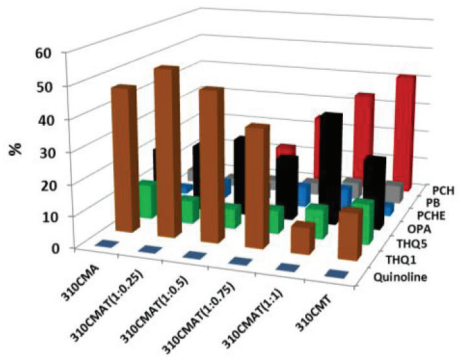
60
50
40
30
20
10
0
%
310CMA
310CMAT(1:0.25)
310CMAT(1:0.5)
310CMAT(1:0.75)
310CMAT(1:1)
310CMT
PCH
PB
PCHE
OPA
THQ5
THQ1
Quinoline